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Hyperfine Interactions and Λ-Type Doubling in the Microwave Spectrum of the NS Radical

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Strong absorption lines due to free NS radicals have been observed by means of Stark modulated microwave spectrometers, in the discharge products of a mixture of nitrogen and sulfur dichloride or sulfur monochloride. The rotational transitions $J = \frac{3}{2} \leftarrow \frac{1}{2}$ in the $^2\Pi_{1/2}$ state as well as $J = \frac{5}{2} \leftarrow \frac{3}{2}$ both in the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states are analyzed to investigate the Λ-type doubling and the hyperfine interactions in two isotopic species $^{14}N^{32}S$ and $^{14}N^{34}S$.

The parity considerations lead to negative sign of the Λ-type doubling parameter α_p, which indicates that the dominant perturbing state is a $^2\Sigma^-$ state not identified yet. Relative magnitudes of hyperfine constants of NS are very similar to those of NO, although their absolute values in the former are consistently smaller than in the latter. The rotational constant $B_0 = 23156.01 \pm 0.16$ MHz obtained in the present analysis, combined with α_e^B from the γ-band analysis, gives an accurate equilibrium internuclear distance $r_e = 1.4938 \pm 0.0002$ Å. The electric dipole moment is determined to be 1.81 ± 0.02 Debye in the $^2\Pi_{1/2}$ state by the Stark effect measurements.

INTRODUCTION

Mulliken and Christy (*1*) have discussed in detail the Λ-type doubling in many diatomic molecules and compared the observed doubling constants with those calculated on the basis of the pure precession hypothesis. They pointed out that the positive sign of the Λ-type doubling constant of NO conflicted with that which would be expected if the interacting state were $A^2\Sigma^+$. Barrow, Drummond, and Zeeman (*2*) reported the same sort of contradiction for NS; the Λ-type doubling constant p in the ground $^2\Pi_{1/2}$ electronic state was determined to be $+0.011$ cm^{-1} (*2*, *3*). It is interesting to point out that the sign of p can be determined, if the "hyperfine doubling," that is, the difference between the hyperfine energy levels of the Λ-type doubling components, is observed. In the present work, positive sign was obtained for p from the hyperfine doubling, and at the same time the accuracy of p was improved by a factor of 100. These results suggest the presence of $^2\Sigma^-$ states which give the main contributions to make the p constant positive.

The hyperfine constants of NO obtained by millimeter-wave spectroscopy

(*4, 5*) or by electron paramagnetic resonance (*6, 7*) were analyzed thoroughly to estimate the distribution of the unpaired electron in the molecule (*8, 9*). In view of these results it is interesting to determine the hyperfine constants of NS and to compare them with those of NO.

Carrington and Levy (*10*) reported the electron-paramagnetic-resonance spectra of the NS in the $^2\Pi_{3/2}$ state in the reaction products of hydrogen sulfide with active nitrogen. Recently Carrington, Howard, Levy, and Robertson (*11*) improved the signal-to-noise ratio considerably by replacing H_2S with sulfur monochloride and Uehara and Morino (*12*) by a microwave discharge through a mixture of sulfur dichloride and nitrogen. The hyperfine constants thus obtained were in good agreement with the present results. However, information obtained from the EPR spectroscopy is confined only to the $^2\Pi_{3/2}$ state, because the molecule in the $^2\Pi_{1/2}$ state is nearly diamagnetic.

In the present work the microwave spectrum of NS in the ground electronic state was observed both for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states and analyzed by taking into account the dependence of the spin–orbit coupling constant A on the internuclear distance, as in the case of ClO reported in a previous paper (*13*). The rotational constants thus obtained were improved very much in accuracy because of the high precision of microwave spectroscopy.

EXPERIMENTAL

A conventional 100 kHz Stark modulated microwave spectrometer was used. OKI 70V11A and 120V10 klystrons were employed as microwave sources. The absorption cell for the measurement in the 69 GHz region was made of parallel plates. The cell was already used in the previous works on the SO (*14*) and ClO (*15*) radicals. The measurements in the region of 115 to 117 GHz were performed by means of a spectrometer at Sagami Chemical Research Center.

The NS radical was produced through a microwave or a radio-frequency discharge in a mixture of nitrogen and sulfur dichloride or sulfur monochloride. The total pressure of the flowing gas was about 0.1 mm Hg.

Dark-brown substance was deposited on the glass wall of the discharge tube and the absorption cell. No attenuation of microwave power was found for this solid deposit. It was almost completely cleaned out by a flow of discharged oxygen gas, with blue chemiluminescence.

THEORY

Although theory of the Λ-type doubling and the hyperfine interactions is well established (*16–18*), there has often been a confusion on the symmetry properties of energy levels, because of different phases chosen by different authors. The discussions given below are to clarify the relation between the parity of the wavefunction and the sign of the Λ-doubling constant or the hyperfine doubling constant d. Total wavefunction is expressed by a product of functions for electronic orbital motion, overall rotation of the whole molecule, and electron spin. The Eulerian angles θ, ψ, φ connecting the molecule-fixed coordinate system with the space-fixed coordinate system are defined according to Nielsen (*19*). The inversion operation is equivalent to the reflection σ_v of the electron coordinates at a vertical plane which contains x and z axes, where z axis is taken along the molecular axis, followed by the two-fold rotation U_2 of the molecule-fixed coordinate system about y axis. The latter operation does not affect the electronic orbital wavefunction, and its operation on the Eulerian angles is

$$\theta \rightarrow \pi - \theta, \quad \psi \rightarrow \pi + \psi, \qquad \text{and} \qquad \varphi \rightarrow \pi - \varphi.$$

The Hund's case (a) wavefunctions are chosen as a basis. In the following discussions, $|\Lambda\rangle$ and $|S\Sigma\rangle$ denote electronic orbital and spin wavefunctions, respectively, and $|J\Omega\rangle$ the wavefunction for overall rotational motion. The transformation properties of the wavefunctions under the inversion $\mathcal{I} \equiv \sigma_v U_2$ are defined after Kopp and Hougen (*20*) as follows:

$$\begin{aligned} \mathcal{I}|\Lambda\rangle &= |-\Lambda\rangle \text{ for } \Lambda \neq 0 \\ \mathcal{I}|\Lambda\rangle &= \pm|\Lambda\rangle \text{ for } \Lambda = 0, \Sigma^{\pm} \\ \mathcal{I}|S\Sigma\rangle &= (-1)^{S-\Sigma}|S-\Sigma\rangle \\ \mathcal{I}|J\Omega\rangle &= (-1)^{J-\Omega}|J-\Omega\rangle. \end{aligned} \tag{1}$$

The basis set is chosen as follows to have a correct parity:

$$|{}^{2S+1}\Lambda_\Omega\,;\, J\Omega;\, \pm\rangle = 2^{-1/2}[|\Lambda\rangle|S\Sigma\rangle|J\Omega\rangle \pm |-\Lambda\rangle|S-\Sigma\rangle|J-\Omega\rangle]. \tag{2}$$

Using the transformation properties defined by Eq. (1), one finds that the parities of the function $|{}^2\Pi_{1/2};J\tfrac{1}{2};+\rangle$ and $|{}^2\Pi_{1/2};J\tfrac{1}{2};-\rangle$ are $(-1)^{J+1/2}$ and $(-1)^{J-1/2}$, respectively. For the Σ states ($\Lambda = 0$), $|{}^2\Sigma^{\pm}_{1/2};J\tfrac{1}{2};+\rangle$ has the parity of $(-1)^p(-1)^{J-1/2}$ and $|{}^2\Sigma^{\pm}_{1/2};J\tfrac{1}{2};-\rangle(-1)^p(-1)^{J+1/2}$, where the factor $(-1)^p$ means $+1$ for ${}^2\Sigma^+$ states and -1 for ${}^2\Sigma^-$ states. Therefore the rovibronic levels are classified into two groups according to their parities $(-1)^{J-1/2}$ or $(-1)^{J+1/2}$. The former will be called "c levels" and the latter "d levels."[1] For the d levels,

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[1] The definitions of "c levels" and "d levels" are somewhat different from those presented by Mulliken (*Rev. Mod. Phys.* **3,** 89 (1931)). He defined one series where the parity of the lowest rotational level was positive as "d levels" in the regular case (a) doublet states and as "c levels" in the inverted case (a), and the other series, the lowest rotational level of which had negative parity as "d levels" in the regular case (a) doublet states and as "c levels" in the inverted case (a). Therefore the definitions by Mulliken and in the present work for "c levels" and "d levels" are contrary to each other for ${}^2\Pi_{1/2}$ in the regular doublet states and for ${}^2\Pi_{3/2}$ in the inverted states, but are the same, for ${}^2\Pi_{1/2}$ in the inverted and for ${}^2\Pi_{3/2}$ in the regular doublet states.

the Hamiltonian matrix is given by

$$\begin{pmatrix} \alpha + \delta & \theta + \zeta & \eta \\ \theta^* + \zeta^* & \beta & \epsilon \\ \eta^* & \epsilon^* & \gamma \end{pmatrix} \tag{3}$$

where each matrix element is that defined by Van Vleck (*16*), except that the phase convention is different. The matrix for the c levels is similar to Eq. (3) but with the changes of the signs before δ and ζ.

It is important to note that α_p and β_p defined by

$$\alpha_p = 4\Sigma(-1)^p \frac{\langle \Pi \mid (A + 2B)L_x \mid \Sigma\rangle\langle \Sigma \mid BL_x \mid \Pi\rangle}{E_\Sigma - E_\Pi} \qquad (4)^2$$

$$\beta_p = 4\Sigma(-1)^p \frac{\mid \langle \Pi \mid BL_x \mid \Sigma\rangle \mid^2}{E_\Sigma - E_\Pi} \tag{5}$$

originate from the terms $\theta\zeta^*$ and $\theta^*\zeta$, and $\zeta\eta^*\epsilon$ and $\zeta^*\eta\epsilon^*$, respectively. On the other hand, as clearly seen from Eqs. (13), (14), and (17) in the paper by Dousmanis, Sanders, and Townes (*17*), W_1 does not contain these terms. It involves the terms $\theta\epsilon\eta^*$, $\theta^*\epsilon^*\eta$, $\delta\theta\zeta^*$, $\delta\theta^*\zeta$ and $\zeta\zeta^*$, $\eta\eta^*$, $\delta\zeta\epsilon\eta^*$, $\delta\zeta^*\epsilon^*\eta$. The former ones $(\theta\epsilon\eta^*, \cdots)$ give rise to

$$\alpha_p' = 4\Sigma \frac{\langle \Pi \mid (A + 2B)L_x \mid \Sigma\rangle\langle \Sigma \mid BL_x \mid \Pi\rangle}{E_\Sigma - E_\Pi} \tag{6}$$

and the latter ones $(\zeta\zeta^*, \cdots)$ to

$$\beta_p' = 4\Sigma \frac{\mid \langle \Pi \mid BL_x \mid \Sigma\rangle \mid^2}{E_\Sigma - E_\Pi} \tag{7}$$

in W_1. Therefore α_p and β_p in W_1 given by Dousmanis, Sanders, and Townes should be replaced by α_p' and β_p', respectively.

According to Dousmanis, Sanders, and Townes (*17*), the splitting of the Λ-type doublet $W_2(J)$ is defined to be the energy difference between the d level and the corresponding c level,

$$W_2(J) = W_d(J) - W_c(J) \tag{8}$$

The explicit formulas are identical with those presented earlier (*13*), and are not reproduced here.

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[2] The transformation properties given in Eq. (1) mean that the matrix elements $\langle \Lambda = -1 \mid L_x \mid \Lambda = 0\rangle$ and $\langle \Lambda = 1 \mid L_x \mid \Lambda = 0\rangle$ should be real, and the following relations are easily derived:

$$\langle \Lambda = -1 \mid L_x \mid \Lambda = 0\rangle = (-1)^{p+1}\langle \Lambda = 1 \mid L_x \mid \Lambda = 0\rangle$$

In the article by Van Vleck, the elements of L_y have been chosen real.

Next, the sign of hyperfine doubling terms should be considered. The definition of the transformation presented in Eq. (1) makes it necessary to change the phase of the matrix elements given by Frosch and Foley (*18*). The hyperfine doubling term for the $^2\Pi_{1/2}$ state is easily calculated to be

$$W_{\mathrm{hf}}^{(\mathrm{d})} = \pm[d(J + \tfrac{1}{2})/2J(J + 1)]\mathbf{I}\cdot\mathbf{J}. \tag{9}$$

The positive sign in front of d applies to the d levels and the negative sign to the c levels. In this connection, the statement that the positive sign applies to the upper Λ-doublet levels, is not always correct, although in all the molecules analyzed so far, the upper Λ-doublet levels are assigned to d levels.

RESULTS

A. ANALYSIS

The NS radical is well characterized by the coupling scheme of Hund's case (a) because of large $\lambda_0 \equiv A_0/B_0$. The energy formulas used in the analysis of the ClO spectra (*13*) can be applied to the present analysis with replacements of α_p and β_p appearing in the effective rotational constants by α_p' and β_p', respectively. The NS radical shows the same pattern of the hyperfine structure as that in NO (*4*, *5*), because of the similarity in the electronic structure. The separation of the hyperfine sub-levels in the $^2\Pi_{1/2}$ state is larger in the upper Λ-doublet components than in the lower. An assumption that the sign of the hyperfine doubling term d is positive leads to the level scheme that the upper members of the doublets are assigned to d levels, as in the case of NO. The Λ-type doubling in the $^2\Pi_{3/2}$ state could not be resolved under the present experimental conditions. Tables I and II list the observed transition frequencies and the differences be-

TABLE I

TRANSITION FREQUENCIES OF THE $^{14}N^{32}S$ IN THE $^2\Pi_{1/2}$ STATE (MHz)

	$J = \tfrac{3}{2} \leftarrow \tfrac{1}{2}$			$J = \tfrac{5}{2} \leftarrow \tfrac{3}{2}$		
	$F' \leftarrow F$	Obs	Δ[a]	$F' \leftarrow F$	Obs	Δ[a]
c-state	$\tfrac{5}{2} \leftarrow \tfrac{3}{2}$	69002.85	0.29	$\tfrac{7}{2} \leftarrow \tfrac{5}{2}$	115153.92	0.17
	$\tfrac{3}{2} \leftarrow \tfrac{1}{2}$	69016.92	0.06	$\tfrac{5}{2} \leftarrow \tfrac{3}{2}$	115156.97	0.16
	$\tfrac{3}{2} \leftarrow \tfrac{3}{2}$	69037.31	−0.13	$\tfrac{3}{2} \leftarrow \tfrac{1}{2}$	115163.07	−0.03
	$\tfrac{1}{2} \leftarrow \tfrac{1}{2}$	69040.17	−0.19	$\tfrac{3}{2} \leftarrow \tfrac{3}{2}$	115185.55	−0.05
	$\tfrac{1}{2} \leftarrow \tfrac{3}{2}$	69060.27	0.33	$\tfrac{5}{2} \leftarrow \tfrac{5}{2}$	115191.07	−0.62
d-state	$\tfrac{1}{2} \leftarrow \tfrac{3}{2}$	69283.13	−0.07	$\tfrac{5}{2} \leftarrow \tfrac{5}{2}$	115489.61	0.06
	$\tfrac{3}{2} \leftarrow \tfrac{3}{2}$	69330.25	−0.07	$\tfrac{3}{2} \leftarrow \tfrac{3}{2}$	115524.82	−0.07
	$\tfrac{5}{2} \leftarrow \tfrac{3}{2}$	69411.35	−0.13	$\tfrac{7}{2} \leftarrow \tfrac{5}{2}$	115556.43	0.39
	$\tfrac{1}{2} \leftarrow \tfrac{1}{2}$	69437.40	−0.27	$\tfrac{5}{2} \leftarrow \tfrac{3}{2}$	115571.20[b]	0.49
	$\tfrac{3}{2} \leftarrow \tfrac{1}{2}$	69484.97	0.17	$\tfrac{3}{2} \leftarrow \tfrac{1}{2}$		−0.82

[a] Δ denotes obs. − calc.

[b] Not included in least-squares fit.

TABLE II

TRANSITION FREQUENCIES OF THE $^{14}N^{32}S$ IN THE $^2\Pi_{3/2}$ STATE (MHz)

$J = 5/2 \leftarrow 3/2$		
$F' \leftarrow F$	Obs.	Δ^a
$5/2 \leftarrow 5/2$	116147.76	−0.02
$3/2 \leftarrow 3/2$	116181.78[b]	2.18
$7/2 \leftarrow 5/2$		0.00
$5/2 \leftarrow 3/2$	116203.61	0.14
$3/2 \leftarrow 1/2$	116214.47	−0.12

[a] Δ denotes obs. − calc.

[b] Not included in least-squares fit.

TABLE III

MOLECULAR CONSTANTS OF THE NS RADICALS IN THE $^2\Pi$ ELECTRONIC STATE (MHz, unless otherwise indicated)[a]

	$^{14}N^{32}S$	$^{14}N^{34}S$
B_{01}	23072.10 ± 0.13	22661.58 ± 0.11
B_{02}	23238.61 ± 0.18	—
D_e	0.028 ± 0.012	—
p_{eff}	397.32 ± 0.40	389.61 ± 0.59
$a + (b + c)/2$	56.35 ± 0.83	—
$a - (b + c)/2$	67.45 ± 0.50	67.02 ± 0.83
d	87.03 ± 0.42	87.22 ± 1.02
eq$Q$	−2.62 ± 0.73	−1.74 ± 1.56
B_0	23156.01 ± 0.16	—
α_p	−198.24 ± 0.38	—
β_p	−0.682 ± 0.002	—
r_e	1.4938 ± 0.0002 Å	—

[a] Uncertainties indicated are three times the standard errors from the least-squares fit.

tween the observed and the calculated. The final values of the parameters determined by a least-squares fitting are given in Table III.

The parameter p_{eff} is expressed, for the molecules approximated as Hund's case (a), as

$$p_{eff} = -2\alpha_p - (\alpha_p - 2\beta_p)|A|/(E_\Sigma - E_\Pi) \qquad (10)$$

where α_p and β_p are defined by Eqs. (4) and (5), respectively. Zeeman's value of p_{eff}, +0.011 cm^{-1} or +330 MHz, is to be replaced by the present more accurate value, +397.32 ± 0.40 MHz. After correcting the second term of Eq. (10) by the same procedure as adopted in the case of ClO (*13, 15*), α_p was obtained to be −198.24 MHz, and β_p was calculated to be −0.682 MHz by the use of Eq. (35)

in Ref. (*13*). The negative sign of α_p indicates that the dominant perturbing state is $^2\Sigma^-$. Therefore, if it is assumed that only one $^2\Sigma^-$ state interacts with the ground $^2\Pi$ state, α_p' and β_p' may be approximated by

$$\begin{aligned} \alpha_p' &= -\alpha_p \\ \beta_p' &= -\beta_p . \end{aligned} \tag{11}$$

The effective rotational constants are defined by

$$\begin{aligned} B_{v1} = B_v - \beta_p' &+ \frac{(B_v - \gamma/2)^2 - B_v \alpha_p}{2B_v - A_v} - 2\epsilon^2 A' \\ &+ 4\epsilon B_e^2 \left[\frac{v+1}{2B_v - A_v - \omega_e} + \frac{v}{2B_v - A_v + \omega_e} \right], \end{aligned} \tag{12}$$

$$\begin{aligned} B_{v2} = B_v - \beta_p' &- \frac{(B_v - \gamma/2)^2 - B_v \alpha_p}{2B_v - A_v} + 2\epsilon^2 A' + 16\epsilon B_e^2/\omega_e \\ &- 4\epsilon B_e^2 \left[\frac{v+1}{2B_v - A_v + \omega_e} + \frac{v}{2B_v - A_v - \omega_e} \right] \end{aligned} \tag{13}$$

where A' denotes $(r \cdot dA/dr)_{r_e}$. The rotational constant B_0 was, therefore, calculated to be $B_0 = 23156.01 \pm 0.16$ MHz from the sum of the two effective rotational constants using the spin–orbit coupling constant A_0,[3] the vibrational frequency ω_e obtained by Zeeman (*3*), the centrifugal distortion constant D_e and the l-uncoupling parameter β_p'. The value of B_0 reported by Zeeman, 0.77058 cm^{-1} or 23101.4 MHz, is, therefore, definitely small by about 50 MHz. Carrington, Howard, Levy, and Robertson (*11*) stated that the rotational constant $B_0 = 0.7722\ \text{cm}^{-1}$ (23 150 MHz) could reduce slight discrepancies between the calculated and the observed frequencies which were present when the rotational constant reported by Zeeman was used in the analysis of the EPR spectra.

From the present value of B_0 and the vibration–rotation constant α_e of 0.0061_2 cm^{-1} ($183._5$ MHz) determined through the analysis of the γ-band systems (*3*), one may calculate the equilibrium rotational constant B_e, and therefore the equilibrium internuclear distance r_e, with sufficient accuracy. If the uncertainty in α_e is assumed to be $\pm 0.0001\ \text{cm}^{-1}$, the equilibrium internuclear distance becomes

$$r_e = 1.4938 \pm 0.0002\ \text{Å},$$

where the uncertainty arising from Planck's constant is also included.

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[3] The spin–orbit coupling constant A of $223.0_3\ \text{cm}^{-1}$ determined by Zeeman should be understood as A_1, because the constant was determined through the analysis of the (0, 1) band. Least-squares analyses both for the (0, 1) and (0, 0) bands on the basis of Eq. (25) and Tables I and II in Ref. (*3*), has led to $A_0 = 222.94 \pm 0.17\ \text{cm}^{-1}$ and $A_1 = 223.09 \pm 0.12\ \text{cm}^{-1}$. This value for A_0 was used in the present analysis.

The rotational constant difference

$$\begin{aligned} B_{01} - B_{02} = {} & 2\,\frac{B_0 - \alpha_p - \gamma + \gamma^2/4B_0}{2 - \lambda_0} - 4\epsilon^2 A' \\ & - D_e\left[4 - \frac{\omega_e}{2B_0 - A_0 - \omega_e} - \frac{\omega_e}{2B_0 - A_0 + \omega_e}\right], \end{aligned} \tag{14}$$

gives an estimate of A'. Though the spin–rotation coupling constant γ is not known, it is estimated to be less than 400 MHz, and the numerator of the first term in the right-hand side of Eq. (14) is thus equal to $(2.296 \pm 0.04) \times 10^4$ MHz. The term $4\,\epsilon^2 A'$ amounts, therefore, to 6.4 ± 2.8 MHz. Using the values of B_e and ω_e, one finds that ϵ becomes 0.635×10^{-3}, and consequently A' is determined to be $130 \pm 56\ \mathrm{cm}^{-1}$.

The spectra are strong enough to observe the lines arising from the $^2\Pi_{1/2}, J = 3/2 \leftarrow 1/2$ transitions of the $^{14}N^{34}S$ in natural abundence (about 4.2%). Table IV lists the observed transition frequencies, and the molecular constants obtained by means of a least-squares fitting are cited in Table III. No differences are observed in the hyperfine coupling constants *d* between the two isotopic species $^{14}N^{32}S$ and $^{14}N^{34}S$.

B. STARK EFFECT

Martix elements necessary for calculating the Stark effect in the $^2\Pi_{1/2}$ electronic state have already been given by Mizushima (*21*). Since the second-order contribution from the adjacent rotational levels is estimated to be less than 1% and is smaller than the experimental uncertainties, it is sufficient to consider only the $\Delta J = 0$ elements. The electric field strength was calibrated by measuring

TABLE IV

TRANSITION FREQUENCIES OF THE $^{14}N^{34}S$ IN THE $^2\Pi_{1/2}$ STATE (MHz)

	$J = 3/2 \leftarrow 1/2$		
	$F' \leftarrow F$	Obs	Δ[a]
	$5/2 \leftarrow 3/2$	67775.33	0.06
	$3/2 \leftarrow 1/2$	67790.37	−0.06
c-state	$3/2 \leftarrow 3/2$	67812.31[b]	1.67
	$1/2 \leftarrow 1/2$		−0.39
	$3/2 \leftarrow 3/2$	68095.64	0.05
	$5/2 \leftarrow 3/2$	68176.35	−0.16
d-state	$1/2 \leftarrow 1/2$	68202.37	0.05
	$3/2 \leftarrow 1/2$	68249.88	0.05

[a] Δ denotes obs. − calc.

[b] Not included in least-squares fit.

TABLE V

ELECTRIC DIPOLE MOMENT IN THE $^2\Pi_{1/2}$ STATE

Transition $F' \leftarrow F$	$\mu(D)$
$\frac{1}{2} \leftarrow \frac{1}{2}$ (*d*)	1.82 ± 0.06
$\frac{3}{2} \leftarrow \frac{1}{2}$ (*d*)	1.80 ± 0.02
$\frac{3}{2} \leftarrow \frac{1}{2}$ (*c*)	1.82 ± 0.04
Mean	1.81 ± 0.02

the Stark shift of the $J = 1 \leftarrow 0$ transition of OCS, where the dipole moment of 0.71521 Debye reported by Muenter was used (*22*). Table V gives the dipole moments obtained from three transitions of $^{14}N^{32}S$. Thus the dipole moment was determined to be 1.81 ± 0.02 Debye by taking the mean value of these three. Carrington, Howard, Levy, and Robertson (*11*) reported the dipole moment $\mu = 1.35 \pm 0.10$ Debye for the $^2\Pi_{3/2}$ electronic state by the electron paramagnetic resonance. The electric dipole moments in the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states are expected to have almost the same value within current experimental accuracy, and the source of large discrepancy between these two measurements is not evident.

DISCUSSION

The parity of each rotational level was determined on the basis of a reasonable assumption that the sign of the hyperfine doubling term *d* was positive. *Ab initio* calculations of the hyperfine coupling constants of NO were made by Lefebvre-Brion and Moser (*8*), and by Lin, Hijikata, and Sakamoto (*9*). All these calculations show that the sign of *d* is positive, as expected from simpler calculations. For the NS radical, reliable wavefunctions are not available to calculate the coupling constant *d* accurately. However, it is reasonable to assume the positive sign of *d* also in NS. The symmetry species, $^2\Sigma^+$ or $^2\Sigma^-$, of the upper state of the γ-band cannot be determined from the analysis of the band alone, but molecular orbital considerations suggest that the state is $^2\Sigma^+$. The parity of each level of the ground state, inferred from this discussion, is identical with that derived by the present analysis of the hyperfine doubling. The sign of the Λ-type doubling parameter α_p could be given from the parity. The negative sign of α_p indicates that the dominant perturbing state was not the $C^2\Sigma^+$ state but an unknown $^2\Sigma^-$. Lofthus and Miescher (*23*) observed the $G^2\Sigma^-$ state of NO, at about 63 000 cm^{-1} above the ground state, and indicated that this state must be a perturbing state, because of a good agreement of the observed Λ-type doubling constant with that calculated by means of the pure precession hypothesis. As for the NS radical, a state analogous to the $G^2\Sigma^-$ of NO may exist, but has not been found yet. It is interesting in this connection to obtain the doubling constants of the excited $^2\Pi$ states. If they were determined both in magnitude and

TABLE VI

MAGNETIC HYPERFINE CONSTANTS OF DIATOMIC FREE RADICALS (in MHz)

	OH[a]	NO[b]	NS	ClO[c]
a[d]	86.0 ± 0.6	84.28 ± 0.52	61.90 ± 0.67	136.34 ± 0.68
b	-119.0 ± 0.4	41.8 ± 6.3		
c	133.2 ± 1.0	-58.8 ± 7.4		
$b + c$		-16.93 ± 1.04	-11.10 ± 1.33	-47.47 ± 1.36
d	56.5 ± 0.4	112.60	87.03 ± 0.42	173.07 ± 0.70
$c = 3\ (a - d)$		-84.9	-75.4	-110.2
$c = -d/2$		-56.3	-43.5	-86.5

[a] H. E. RADFORD, *Phys. Rev.* **126,** 1035 (1962).

[b] Refs. (*4*) and (*7*).

[c] Ref. (*13*).

[d] $a = 2g_N\mu_N\beta\langle 1/r^3\rangle, b = 2g_N\mu_N\beta\langle \frac{8\pi}{3}\psi^2(0) - (3\cos^2\chi - 1)/2r^3\rangle, c = 3g_N\mu_N\beta\langle (3\cos^2\chi - 1)/r^3\rangle,$
$d = 3g_N\mu_N\beta\langle \sin^2\chi/r^3\rangle.$

sign, they would give important information about the position of the $^2\Sigma$ states. Narasimham and Srikameswaran (*24*) analyzed the $B^2\Pi$–$X^2\Pi$ band systems of NS. By using their frequencies of Λ-type doublings in the higher J-lines of the (7,0) and (8,0) bands, we attempted to derive the Λ-type doubling constant of the upper state, assuming the ground-state constants obtained in the present work, but it was found unsuccessful because of insufficient accuracy and also of possible resonance effects.

Table VI compares the hyperfine constants for the NS radical with those for a few other free radicals investigated by means of microwave spectroscopy or gas-phase electron-paramagnetic resonance spectroscopy. If the single configuration approximation is adopted, $2d/3a$ should be $4/5$ in these free radicals where unpaired electron occupies a p_π orbital. The consideration of configuration interaction reduced the discrepancy in this ratio between the observed and the calculated for the NO (*8*).

The single configuration approximation gives the following two relations

$$c = 3(a\text{–}d) \tag{15}$$

$$c = -d/2. \tag{16}$$

The values of c obtained from these two relations are also compared in Table VI. The hyperfine coupling constants of the OH radical could not be explained by the single configuration approximation. The c constant of NO calculated from Eq. (16) is equal to the observed. Unfortunately, the approximation cannot be tested on the NS and ClO radicals. In order to determine the b constants separately from c the accuracy of frequency measurement should be improved by a factor of ten.

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